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Composition dependence of the optical band gap and thermal diffusivity in Ge-As-Se glasses

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Abstract : The composition dependence of the optical band gap (E_0) and thermal diffusivity (α) of bulk $Ge_xAs_{10}Se_{90-x}$ and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses have been measured using photoacoustic technique. The variation of E_0 and α with the average coordination number $\langle r \rangle$ shows a threshold maximum around $\langle r \rangle = 2.67$. The anomalous behaviour is explained on the basis of the changes in network topology due to the formation and development of layered structures in these systems

Keywords : Chalcogenide glasses, optical band gap, thermal diffusivity

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1. Introduction

The role of microscopic topology in determining the properties of glass-forming compounds has been explored theoretically for the past several years. The concept of an average atomic coordination number has been used by Phillips [1] in constraint counting arguments explaining the strong glass-forming tendency of certain alloy compositions. These ideas have been later refined by Thorpe and coworkers [2,3,4] who predicted that a rigidity percolation transition from a soft to a rigid structure should occur at an average coordination number $\langle r \rangle = 2.4$. Later, Tanaka [5,6] extended Phillips' ideas, which are based purely on short-range interactions, to a two-dimensional glassy structure and taking medium-range interactions also into account it was shown that the average coordination number of glasses having stable layered structure is $\langle r \rangle = 2.67$.

The large glass-forming region of ternary Ge-As-Se system makes it possible for a given value of the average coordination number $\langle r \rangle$ to be realized with a continuous range of chemical compositions, allowing purely topological effects to be distinguished from chemical effects. In the three-component Ge-As-Se system, selenium will react primarily with

germanium and produce structural units of $GeSe_{4/2}$. When germanium is introduced into arsenic selenides, gradual changes in composition take place in the system forming $GeSe_{4/2}$ and $AsSe_{3/2}$. Introduction of germanium into the glassy arsenic selenide can be accompanied also by the formation of the complex structural units $AS_2Ge_{4/2}Se_{4/2}$ of the glass forming Ge-As-Se system. Approximate thermochemical calculations indicate that in the three component Ge-As-Se system, there can be several sections with different physical and chemical properties. There can be sections in which the structure is determined mainly by bonds of the selenium type [7].

Recently, experimental reports correlating the elastic constants of Ge-As-Se glasses with $\langle r \rangle$ suggest the occurrence of a threshold at $\langle r \rangle = 2.4$ [8]. But this data do not match with the previous report by Tillie and coworkers [9] and their samples contained oxygen inclusions. Hence, their report could not be taken as a conclusive evidence for the observation of a threshold at $\langle r \rangle = 2.4$. The persistent infrared spectral-hole burning studies of the effects of network topology on low temperature relaxation in Ge-As-Se glasses show no indication of a rigidity transition or any other unusual features at $\langle r \rangle = 2.4$ [10]. Another study of the $\langle r \rangle$ dependence on excess heat capacity ΔC_p measured at T_g shows minimum at $\langle r \rangle = 2.4$, whereas excess expansion coefficient $\Delta\alpha$ shows absence of any anomaly at $\langle r \rangle = 2.4$ in selected Ge-As-Se glasses [11]. Their studies on the $\langle r \rangle$ dependence of glass transition temperature T_g shows no significant variation at $\langle r \rangle = 2.4$.

In order to clarify the disparity in the reported values of the threshold in Ge-As-Se systems, experimental techniques which are sensitive to probe the composition dependence should be used. The composition dependence of the optical band gap E_0 and thermal diffusivity α of two sets of glasses belonging to the Ge-As-Se system investigated using photoacoustic (PA) technique are reported in this paper.

2. Experimental

The PA spectrometer used for the present investigations consists of a powerful Xe lamp, a source monochromator, a mechanical chopper, a home-made small volume PA cell and lock-in amplifier to process the PA signal detected by an electret microphone kept inside the PA cell. The details of the PA spectrometer are reported elsewhere [12]. Powdered samples have been used for recording the PA absorption spectra. The chopping frequency used is 22 Hz for absorption measurements. The optical band gap E_0 is determined by measuring the variation of the normalized PA signal with incident wavelength. The PA spectrum obtained for a highly absorbing carbon black sample is used to normalize the spectrum obtained for each sample.

The compositions studied in this work can be represented as $Ge_xAs_{10}Se_{90-x}$ (with x = 5, 10, 15, 20, 25, 28.5, 30, 35 and 40) and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ (with x = 10, 20, 26.7, 30, 40, 44, 50 and 60). The compositions have been chosen to produce an average atomic coordination $\langle r \rangle$ ranging from 2.15 to 2.9. The samples are prepared by the well established melt-quenching technique. Identical preparation conditions have been followed while preparing all the samples. This is necessary because any change in the preparative conditions may effect the properties of the glasses. The amorphous nature of the samples has been checked by X-ray diffractometry.

Table 1. The glass composition, average coordination number <r> and optical band gap E_0 of the two families of Ge-As-Se glasses.

No.	Composition Ge : As : Se	< r >	E_0(eV)
1	5 : 10 : 85	2.20	1.98
2	10 : 10 : 80	2.30	2.00
3	15 : 10 : 75	2.40	2.07
4	20 : 10 : 70	2.50	2.14
5	25 : 10 : 65	2.60	2.27
6	28.5 : 10 : 61.5	2 67	2.33
7	30 : 10 : 60	2.70	2.32
8	35 : 10 : 55	2.80	2.25
9	40 : 10 : 50	2.90	2.04
10	5 : 5 : 90	2.15	1 98
11	10 . 10 : 80	2.30	2.00
12	13.35 : 13.35 : 73.3	2.40	2.02
13	15 : 15 : 70	2 45	2.05
14	20 20 : 60	2.60	2.12
15	22 : 22 : 56	2.67	2.14
16	25 : 25 : 50	2.75	2.06
17	30 : 30 · 40	2.90	1.97

The variation of the PA signal amplitude with chopping frequency is measured to determine the thermal diffusivity of each sample. The characteristic frequency f_c at which the slope of the curve changes as the sample goes from a thermally thick to a thermally thin regime can be determined from the log-log plots of the PA signal amplitude versus chopping frequency. The procedure is described in detail elsewhere [13]. The thermal diffusivity α is calculated using the relation $\alpha = f_c l^2$ where l is the sample thickness.

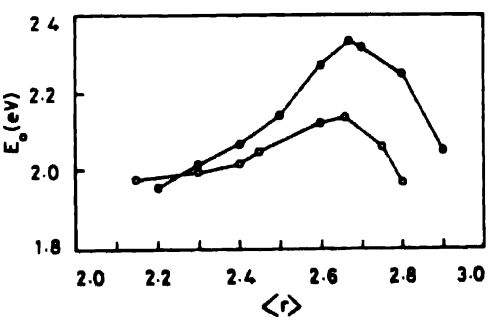

Figure 1. Variation of optical band gap E_0 with average coordination number <r> for Ge-As-Se glasses (●) $Ge_xAs_{10}Se_{90-x}$ (0) $(Ge_{0.5}As_{0.5})_xSe_{100-x}$.

3. Results

The glass compositions alongwith their corresponding <r> and E_0 values are tabulated in Table 1. The variation of the optical band gap of these glasses with <r> is shown in Figure 1.

It can be seen that the optical band gap increases gradually as $\langle r \rangle$ is increased and shows maxima around $\langle r \rangle = 2.67$ for both $Ge_xAs_{10}Se_{90-x}$ and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses. Beyond $\langle r \rangle = 2.67$ the optical band gap decreases gradually.

Table 2. The glass composition, average coordination number $\langle r \rangle$, characteristic frequency f_c, thickness l and thermal diffusivity α of the two families of Ge-As-Se glasses.

No.	Composition Ge : As : Se	$\langle r \rangle$	f_c (Hz)	l (μm)	α (10^2 c m^2/s)
1	5 : 10 : 85	2.20	87.86	90	0.712
2	10 : 10 : 80	2.30	73.23	100	0.732
3	15 : 10 : 75	2.40	95.79	100	0.958
4	20 : 10 : 70	2.50	104.4	100	1.044
5	25 : 10 : 65	2.60	110.6	100	1.106
6	28.5 : 10 . 61.5	2.67	113.8	100	1.138
7	30 : 10 : 60	2.70	105.3	100	1.053
8	35 : 10 : 55	2.80	97.16	100	0.972
9	40 : 10 · 50	2.90	90.40	100	0.904
10	5 : 5 : 90	2.15	72.24	100	0.722
11	10 . 10 . 80	2.30	73 23	100	0.732
12	13.35 : 13 35 · 73.3	2.40	80.52	100	0.805
13	15 : 15 · 70 : 2.45	2.45	90.42	100	0.904
14	20 · 20 : 60	2.60	90.42	110	1.094
15	22 · 22 · 56	2.67	95.76	110	1.159
16	25 : 25 : 50	2.75	90.42	110	1.094
17	30 . 30 · 40	2.90	86.60	110	1 048

The log-log plots of the PA signal amplitude versus chopping frequency of the samples investigated are shown in Figures 2 and 3. The slope of the curve changes at the characteristic frequency f_c because for $f < f_c$ the heat generated at the surface of the sample propagates into the backing medium. Table 2 shows the glass composition, $\langle r \rangle$, f_c, l and α of each of the samples investigated. The variation of α with $\langle r \rangle$ is plotted in Figure 4. As $\langle r \rangle$ is increased, α increases gradually and shows a threshold maximum around $\langle r \rangle = 2.67$

4. Discussion

In order to understand the variation of E_0 with $\langle r \rangle$ in Ge-As-Se glasses, it is necessary to have an idea of the single covalent bond energy of the various bonds present in the network. The single bond energies of the various bonds in the network, namely, Ge-Ge, As-As, Se-Se, Ge-As, Ge-Se and As-Se, calculated by the procedure of Pauling [14,15,16] are 49.1, 47.7, 44.0, 46.6, 55.2 and 51.3 K cal/mol respectively. In Se-rich glasses of the Ge-As-Se system, the two-fold coordinated Se will form flexible chains in the glass network. The addition of the three-fold coordination element As and the four-fold coordinated Ge results in branching and cross-linking of these chains. These configurational changes result in the

formation of a two-dimensional structure which is stabilized by the medium range intermolecular interactions. In both $Ge_xAs_{10}Se_{90-x}$ and $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses, an increase in Ge concentration, which corresponds to an increase in $\langle r \rangle$, increases the possibility for the formation of more Ge-Se bonds. Since the bond energy of Ge-Se bond is higher than all the other possible bonds in the system, the average bond energy of the system increases. According to Kastner's model [17] for band structure of chalcogenide glasses, an increase in the average bond energy of the system tends to increase the energy of the conduction band edge. This effectively increases the optical band gap of the system.

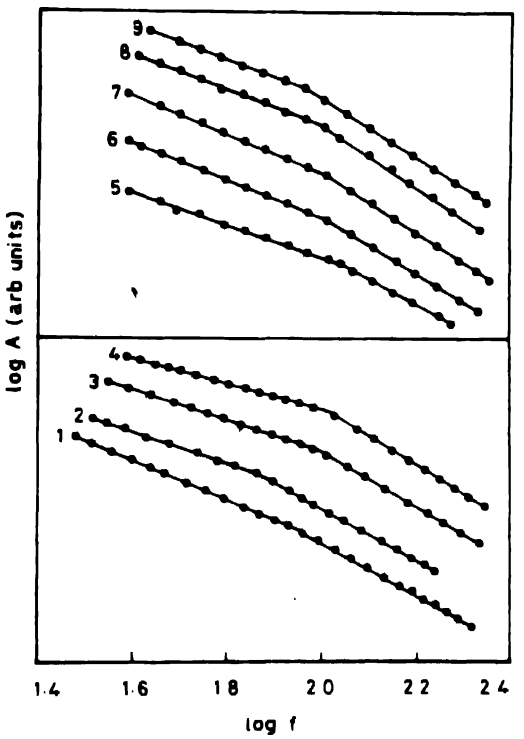

Figure 2. Log-log plot of PA amplitude with chopping frequency of $Ge_xAs_{10}Se_{90-x}$ glasses :

(1) $Ge_5As_{10}Se_{85}$ (2) $Ge_{10}As_{10}Se_{80}$ (3) $Ge_{15}As_{10}Se_{75}$
(4) $Ge_{20}As_{10}Se_{70}$ (5) $Ge_{25}As_{10}Se_{65}$ (6) $Ge_{28.5}As_{10}Se_{61.5}$
(7) $Ge_{30}As_{10}Se_{60}$ (8) $Ge_{35}As_{10}Se_{55}$ (9) $Ge_{40}As_{10}Se_{50}$.

The optical band gap attains a maximum value around $\langle r \rangle = 2.67$. The 2-*d* layered structure is fully developed at this composition and the system goes over to a rigid 3-*d* structure beyond this composition. The cross-linking of the layered structure and the formation of the 3-*d* structure beyond this composition changes the interaction between lone pair *p* electrons which can broaden the lone pairband resulting in a gradual decrease of optical band gap. This could be the reason for the gradual decrease in E_0 beyond the compositions

corresponding to $\langle r \rangle = 2.67$. The occurrance of a maximum around $\langle r \rangle = 2.67$ in these glasses supports the idea of a structural phase transition at $\langle r \rangle = 2.67$ as suggested by Tanaka [5].

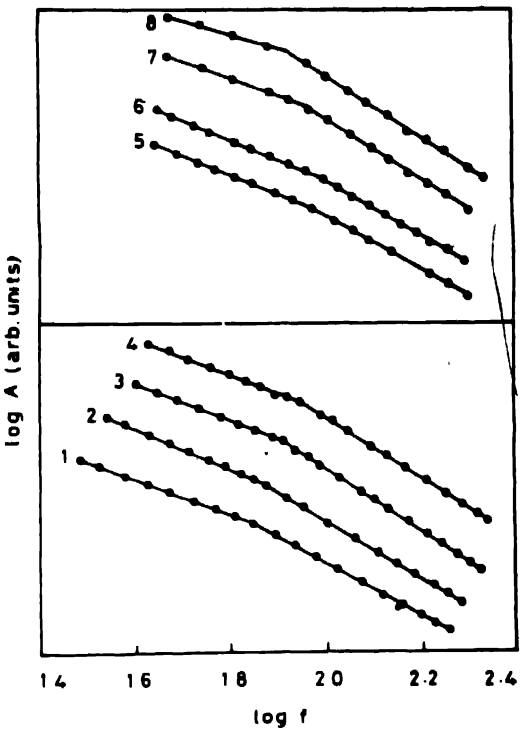

Figure 3. Log-log plots of PA amplitude with chopping frequency of $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ glasses :

(1) $Ge_5As_5Se_{90}$ (2) $Ge_{10}As_{10}Se_{80}$

(3) $Ge_{13.35}As_{13.35}Se_{73.9}$ (4) $Ge_{15}As_{15}Se_{70}$

(5) $Ge_{20}As_{20}Se_{60}$ (6) $Ge_{22}As_{22}Se_{56}$

(7) $Ge_{25}As_{25}Se_{50}$ (8) $Ge_{30}As_{30}Se_{40}$

The variation of α with $\langle r \rangle$ can be interpreted in terms of the change in network topology and dimensionality. It can be inferred that α increases as the 2-*d* layered structure develops through the cross-linking of Se atom chains. This change in dimensionality as $\langle r \rangle$ is increased reduces the flexibility of the network as it goes over to a 3-*d* rigid structure. The maximum value of α around $\langle r \rangle = 2.67$ could be attributed to the formation of layered structure and a medium range order fully getting developed through intermolecular interactions and the system tending to form a 3-*d* structure. The slight decrease in α beyond $\langle r \rangle = 2.67$ may be due to the large number of bonding defects present in the 3-*d* network. Since α is directly related to thermal conductivity, the threshold maximum in α occurring

around $<r> = 2.67$ may be a signature of the development of a more ordered rigid structure at this composition.

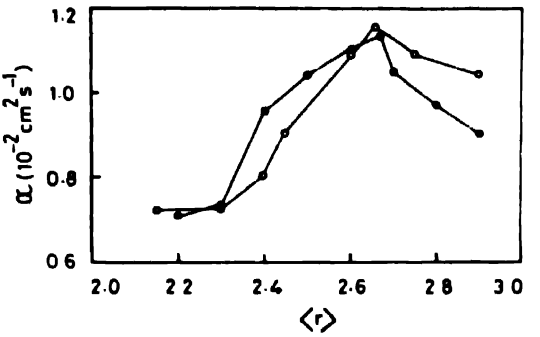

Figure 4. Variation of thermal diffusivity with average coordination number $<r>$ for Ge-As-Se glasses ·
(●) $Ge_xAs_{10}Se_{90-x}$ (0) $(Ge_{0.5}As_{0.5})_xSe_{100-x}$ ·

5. Conclusion

The observed behaviour of Ge-As-Se system shows that the average coordination number $<r>$ is an important parameter to understand the properties of network glasses and is valid even for complex systems like Ge-As-Se. The absence of any observable change in optical band gap or thermal diffusivity in these systems at $<r> = 2.4$ suggests that short-range interactions alone is not sufficient to fully account for the structural properties of these glasses. The observed maxima around $<r> = 2.67$ indicates that medium-range interactions play an important role in determining the network topology in these glasses, as suggested by Tanaka [5]. The present studies establish the sensitivity of thermal diffusivity to rigidity percolation in covalent network glasses.

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